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The electronic structure of colossal magnetoresistive manganites

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Abstract

The ferromagnetic manganites $A_{1-x}B_xMnO_3$ (A a trivalent element and B divalent) have been the subject of intensive study in the past few years. These manganites exhibit colossal magnetoresistance (CMR), i.e. their resistance can drop several orders of magnitude under influence of an external magnetic field. Electronic structure calculations show that these manganites are half-metallic: they are conducting for one spin direction exclusively. The possible relation between half-metallic magnetism and colossal magnetoresistance is discussed. Copyright © 1998 Elsevier Science B.V.

There is considerable interest in large negative magnetoresistance. Early developments were in the area of metallic multilayers [1]. These multilayers consist of alternate stacking of ferromagnetic and non-magnetic metals. The exchange coupling between the ferromagnetic layers takes place through the non-magnetic layers. It can be tuned by the variation of the thickness of the non-magnetic layer to be (weakly) antiferromagnetic.

The direction of the magnetization of the magnetic layers can be forced to be parallel by an external magnetic field. A large reduction in the resistance results. This phenomenon was called "giant" magnetoresistance. While the details of the explanation of the giant magnetoresistance is still an area of active research, it is worthwile remarking here that the asymmetry of the electronic structure for the two spin directions at the Fermi energy for the magnetic layer is a crucial ingredient in any theory. The largest asymmetry possible is found in the so-called half-metallic ferromagnets, systems which are metallic for one spin direction exclusively [2].

Considerable larger negative magnetoresistances are found in the quaternary manganites $A_{1-x}B_xMnO_3$ where A stands for a trivalent metal (La, rare earth) and B is a divalent metal (Ca, Sr, Ba) [3]. Magnetoresistances of 10^6% [4] and higher have been reported ("colossal" magnetoresistance). This paper reports on the electronic structure of one of these materials and the possible relation with the colossal magnetoresistance.

We focus on the compound $La_{1-x}Ca_xMnO_3$, which has been studied extensively experimentally. The magnetic ordering of $La_{1-x}Ca_xMnO_3$ at low temperatures depends on the doping. $La_{1-x}Ca_xMnO_3$ is an antiferromagnetic insulator for $x < 0.2$ and $x > 0.5$, while it is a ferromagnet for $0.2 < x < 0.5$. In and near the ferromagnetic regime the colossal magnetoresistances occur most strongly. Manganites with other elements A and B sometimes have a more complex phase diagram. But in general they all have insulating end points $x = 0$ and $x = 1$ (though not always

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antiferromagnetic but sometimes with a canted spin structure) and a ferromagnetic intermediate regime.

The crystal structure of colossal magnetoresistive manganites is basically a simple perovskite. However, depending on the specific elements A and B the perovskite structure can be distorted, leading to a wide variation in reported crystal structures such as cubic, orthorhombic, tetragonal and rhombohedral. For instance, $CaMnO_3$ is cubic while $LaMnO_3$ has a strongly distorted pervoskite structure with orthorhombic symmetry. In the intermediate region the structure is either an undistorted (cubic) or slightly distorted (orthorhombic) perovskite.

A special case is the $x = 0.5$ compound, for several reasons. First of all, it has a complex temperature dependent magnetic behaviour [5]. $La_{0.5}Ca_{0.5}MnO_3$ orders ferromagnetically at 220–230 K, but the magnetic ordering changes to antiferromagnetic at 150–180 K. Second, the FM–AFM transition is accompanied by a structural transition. There is some controversy about the exact crystal structure of $La_{0.5}Ca_{0.5}MnO_3$. Some authors reported a cubic crystal [4], others an orthorhombic one [5], the distortion of the perovskite structure being small in the FM phase and somewhat bigger in the AFM phase. And third, for this special value of x charge ordering can occur.

We now present the calculations on $La_{1-x}Ca_xMnO_3$. The doping of La by Ca can – in a calculation – only be performed by considering a unit cell consisting of several formula units $LaMnO_3$ and replacing one or more La atoms by Ca atoms. For general values of the doping x this results in very large unit cells and elaborate calculations. Therefore we concentrate on $La_{0.5}Ca_{0.5}MnO_3$. Keeping in mind the controversy about the crystal structure of this compound the crystal structure is assumed to be cubic. The substitution of La by Ca was performed by taking two cubes of the perovskite $LaMnO_3$ above each other and replacing one La atom by a Ca atom, resulting in a tetragonal unit cell with $c = 2a$. Later we will discuss the influence of the crystal structure on the electronic structure in manganites.

The calculations were performed with the full potential LAPW method [6], i.e., no shape approximations to the potential were assumed. The LAPW method is based upon the density functional theory (DFT), which is in principle exact but needs an approximation to the exchange–correlation energy to become numerically feasible. The generalized gradient approximation (GGA) [7] was used, but a comparison is made with standard calculations within the local density approximation (LDA) [8], in order to indicate the small but important difference in the results between the two approximations in this system. For details on the calculation we refer to [9].

The total density of states (DOS) of ferromagnetic $La_{0.5}Ca_{0.5}MnO_3$ is shown in Fig. 1. The zero energy is the Fermi energy. The bands between 7.5 and 1.5 eV below the Fermi energy have primarily oxygen $2p$ character. Around $1 - 1.5$ eV below the Fermi energy lie the spin up Mn t_{2g} bands. The Fermi energy crosses a broad spin up band of manganese e_g orbitals strongly mixed with oxygen 2p orbitals. There are no spin down states at the Fermi energy, since the Fermi energy lies in a gap of 1.5 eV between the oxygen 2p states and the minority conduction band. This means that $La_{0.5}Ca_{0.5}MnO_3$ is half-metallic: metallic for the majority spin electrons but semiconducting for the minority electrons.

We now emphasize the importance of GGA in this system. An LDA calculation leads to a similar picture concerning the position of the oxygen 2p-states and the manganese 3d-states. The most important difference is the minority conduction band which lies slightly lower in energy in the LDA case as compared with the GGA picture. As a consequence the gap between the oxygen 2p-states and the minority conduction band has decreased to 1.4 eV, and, more importantly, the Fermi energy lies now in the conduction band. This means that the LDA calculations do not result in a half-metallic electronic structure, but just in a metallic one. Previous LDA calculations also showed this metallic picture of the manganites, which was called "nearly" half-metallic [10]. Further improvements like self-interaction correction (SIC) could enhance the half-metallic character, because SIC leads possibly to energetically lower occupied states, an effect which is stronger when more localized the bands are. In the manganites this would lead to a larger band gap and

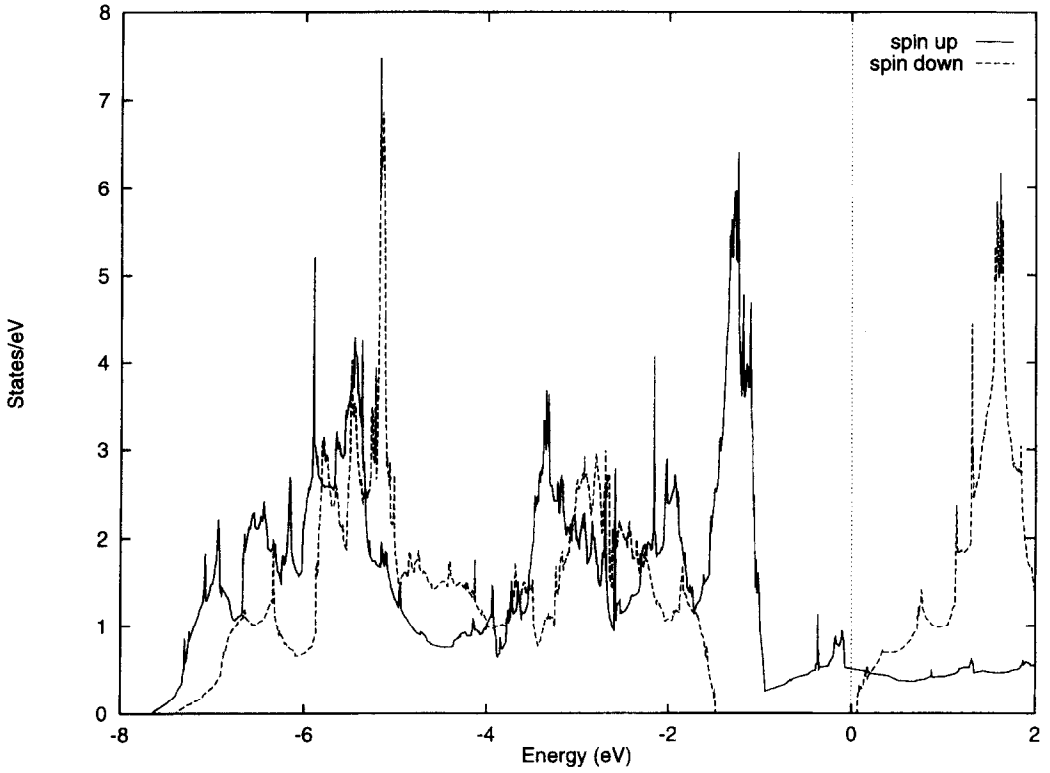

Fig. 1. Total DOS of ferromagnetic $La_{0.5}Ca_{0.5}MnO_3$ calculated within GGA.

a Fermi energy well below the minority conduction band.

At low temperature $La_{0.5}Ca_{0.5}MnO_3$ is antiferromagnetic. We calculated A-type AFM $La_{0.5}Ca_{0.5}MnO_3$ in the same crystal structure as in the FM phase. The total energy of the AFM phase is lower in energy (9 meV per unit cell) than the FM total energy. Though the A-type antiferromagnetic structure is not of the experimentally found type, it is clear that the FM phase is not the ground state, in agreement with experiment.

The total DOS (Fig. 2) shows that AFM $La_{0.5}Ca_{0.5}MnO_3$ is metallic, in disagreement with the experimentally known transport properties, which indicate that it is insulating. Several aspects can influence the conductivity here. First, while the crystal structure in the FM phase is a perfect or only slightly distorted perovskite, it is more distorted in the AFM phase. Second, the AFM phase is in fact of the complex CE-type [11]. Third, it is well known that at $x = 0.5$ in the AFM phase of $A_{1-x}B_xMnO_3$ charge ordering can occur [12].

It is not unreasonable to expect that ferromagnetic manganites with $x < 0.5$ are also half-metallic. Previously published calculations revealed the electronic structure of $x = \frac{1}{3}$ and $x = \frac{1}{4}$ compounds of $La_{1-x}Ca_xMnO_3$. They showed ordinary metallic behaviour, but these calculations were performed within LDA. With the Fermi energy lying just at the bottom of the minority conduction band it is expected that improvements over LDA will give truly half-metallic properties. Half-metallic magnetism could give an explanation for the colossal magnetoresistance, as we will see later.

We now address the question of the origin of the half-metallic behaviour in these manganites and the comparison with earlier half-metallic systems. The explanation of the half-metallic behaviour in the first compounds recognized as such (NiMnSb) [2] depends on both the crystal structure and the chemical

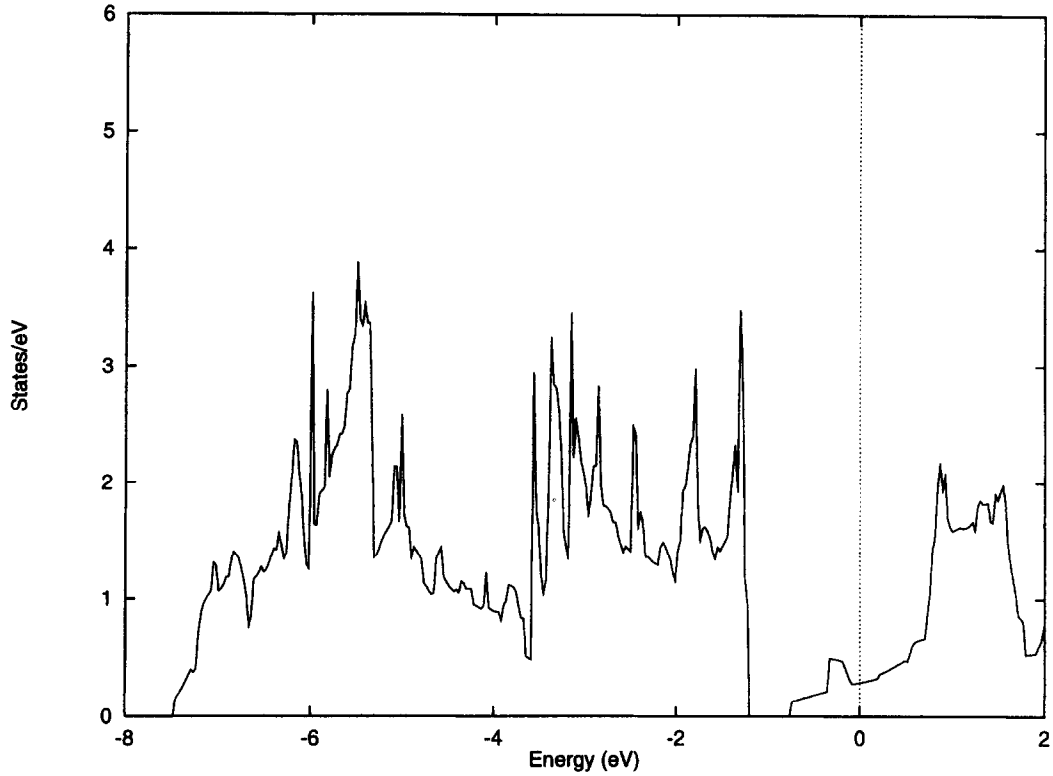

Fig. 2. Total DOS of A-type antiferromagnetic $La_{0.5}Ca_{0.5}MnO_3$.

composition. The crystal structure is pseudo-isostructural with zincblende, while the minority spin direction is iso-electronic with GaAs. The bandstructure, gap, bonding, etc., for the minority spin direction of NiMnSb is typical that of a III–V semiconductor, while for the majority spin the compound behaves like an alloy. Thus the half-metallic properties are quite subtle, depending on both the structure and the composition.

A quite distinct category may exist in the limit of narrow band width materials. In the case of an exchange and crystal field splitting, etc., in access of the band width one can expect half-metallic magnetism to occur frequently. However, whether systems in this limit still conduct or are Mott insulators is questionable. Recent work on the archetype in this category, Fe_3O_4 [13], contradicts earlier predictions of half-metallic properties [14].

A third category of half-metallic materials is in the area of strong magnetic ionic compounds. Strong magnetism is defined by a situation that a hypothetical increase in the exchange splitting does not lead to an increase in magnetic moment, i.e., the majority sub-shell is full or the minority empty. An example of a strong magnetic metal is Ni. But of course Ni shows hardly any spin polarization in the conduction because the mobile 4s, 4p electrons are hardly polarized. But exactly these itinerant electrons are transferred to the electronegative species if one forms an ionic compound, filling up a p-shell and thus disabling these electrons to conduct. Half-metallic behaviour results. The archetype of the third category of half-metallic magnetism is CrO_2 [15], but also the manganites fall into this category.

We now address the possible relation between half-metallic magnetism and colossal magnetoresistance. At zero temperature a half-metallic ferromagnet is uniformly magnetized in one direction. The majority electrons take care of good conduction. At non-zero temperature domains are formed with magnetizations

in other directions. If the half-metallic properties within these domains are preserved, walls between domains of opposite magnetization are insulating.

The correlation length, defined as the average size of domains with magnetization opposite to the total magnetization, increases if the temperature increases and diverges at T_C. Therefore, majority electrons have, with increasing temperature, a decreasing number of percolating paths between the domains with opposite magnetization, which causes the resistivity to increase.

An external magnetic field forces the magnetization to point uniformly in one direction again and therefore lowers the resistivity, resulting in magnetoresistance. Statistical mechanical calculations have confirmed this explanation and have even reproduced the temperature dependent behaviour above the Curie temperature [16].

The mechanism of decreasing percolating paths has a stronger effect on the resistivity, the lower the dimensionality of the system. This is in agreement with experiments which show that thin films exhibit larger magnetoresistances than bulk samples. And it is also in agreement with experiments on layered manganite perovskites $(A, B)_{n+1}Mn_nO_{3n+1}$, which are built by stacking of n-layers of $(A, B)MnO_3$, separated by insulating AO layers. The conduction occurs primarily within the pseudo-two-dimensional n-layers and indeed are the highest CMR values found for the lowest n [17].

The occurrence of colossal magnetoresistance in half-metallic ferromagnetic Heusler alloys like NiMnSb has not been reported, to our knowledge, and is also not expected. There are two reasons for this. First, the charge carriers in NiMnSb have primarily Sb-5p character, which shows a large spin–orbit interaction. Therefore spin-flip scattering in the interface between domains of opposite magnetization would break down the mechanism of half-metallic magnetism causing CMR. And second, the charge carriers in the Heusler alloys are almost free electron like and therefore much more delocalized than the charge carriers in the manganites. As a consequence the interfaces between domains are very sharp in the manganites, but probably substantially thicker in the Heusler alloys.

Colossal magnetoresistance in CrO_2, however, is not improbable a priori but experiments on magnetoresistance in CrO_2 have not been reported to our knowledge.

In conclusion, we presented electronic structure calculations which show that ferromagnetic manganites are half-metallic. We discussed the possible relation between half-metallic magnetism and the occurrence of colossal magnetoresistance.

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